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REPORT NUMBER 6

THE USE OF POLYMER UNZIPPING FOR THE
DETECTION OF BIOLOGICALLY ACTIVE AGENTS

Sixth Quarterly Progress Report

by

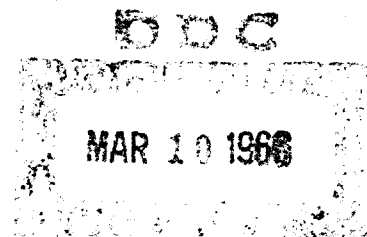Edward B. Dismukes

February 28, 1966

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FOREWORD

The research described in this report was authorized under Task 1A012501B02802, Basic Research in Life Sciences, Chemical. The work was conducted between October 12, 1965, to January 12, 1966. The experimental data are contained in Notebook 3763.

Acknowledgments

The laboratory work described in this report was conducted by Mr. Marion Kirk and by various members of the Analytical Chemistry Section staff - in particular, Mr. James C. Gillespie, Mrs. Frances P. Dean, Mrs. Martha C. Thorpe, and Mrs. Ruby H. James. Dr. Joseph L. Greene, Jr., assisted in planning the polymerization experiments, and Dr. William C. Coburn, Jr., assisted in interpreting infrared and nuclear magnetic resonance spectra.

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DIGEST

The over-all purpose of the research discussed in this report is to determine the feasibility of detecting biologically active agents by their initiation of the depolymerization of certain polymers in a rapid unzipping chain mechanism. Continued work on polymers of n-heptaldehyde has been done, since preliminary results indicated that these polymers were promising for use in detection.

Various kinds of information presented in this report show convincingly that linear polyacetals have been obtained by polymerizing heptaldehyde. This conclusion is based especially on infrared and nuclear magnetic resonance spectral properties of both the polymers synthesized and the monomeric residues obtained by degrading the polymers. It is also supported by determinations of intrinsic viscosity and molecular weight.

Acetate-capped polymers are much more stable than uncapped polymers under most of the conditions investigated. The depolymerization of acetate-capped polymers appears, however, to be catalyzed by surface effects in certain types of infrared cells used for spectral studies. This effect may be caused by end groups besides acetate, for which there is some spectral evidence. Uncapped polymers have been found to depolymerize quite rapidly under certain conditions, as a result of factors that are not specifically identified at present. Partial depolymerization occurs during storage at low temperatures, and the polymer residues remaining after storage appear to depolymerize much more rapidly in solution at room temperature than the freshly prepared materials. The monomeric impurity formed during storage, or an acid impurity formed by air oxidation of the monomer, may catalyze decomposition; alternatively, the reduced molecular weight may account for the more rapid decomposition. Depolymerization appears to be faster in carbon tetrachloride than in chloroform. The main effort in continuing this research will be to identify the factors responsible for rapid depolymerization of uncapped polymers.

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THE USE OF POLYMER UNZIPPING FOR THE
DETECTION OF BIOLOGICALLY ACTIVE AGENTS

I.   INTRODUCTION AND SUMMARY

     This is the sixth report on a study to determine the
feasibility of detecting biologically active agents by their
initiation of the depolymerization of appropriate polymers in
a rapid unzipping chain mechanism.*

     Polymers of n-heptaldehyde are now being investigated.
These polymers, like other polyacetals made from different
aldehyde monomers, are subject to depolymerization when they are
prepared with hydroxyl end groups. On the other hand, these
polymers are stabilized by capping, the conversion of hydroxyl
groups to other types of end groups, such as acetate. Polymers
capped with groups that are degraded specifically by biologically
active agents could theoretically be used to detect these agents
with high sensitivity, since a great many molecules of monomer
could be produced by a single molecule of agent.

     In this investigation, the present effort is to characterize
the fundamental properties of heptaldehyde polymers with acetate
and hydroxyl end groups. Acetate-capped polymers are being
studied since they are easily prepared polymers of a relatively
stable type, which are useful as reference materials in charac-
terization studies. Uncapped polymers with hydroxyl end groups
are of interest, since studies of their depolymerization rates
and mechanism will give insight on the ultimate feasibility of
the proposed detection of biologically active agents.

     Information based especially on studies of osmometric,
viscometric, and spectral properties of materials prepared in
this program leaves no doubt that these materials are linear
acetal polymers of heptaldehyde, with number-average molecular
weights of a few thousand. Thus far, little exact information
on molecular weights is available; however, it appears that this
information can be obtained directly on capped polymers by vapor-
pressure osmometry and perhaps light scattering also, and that
estimates of molecular weights can be obtained for uncapped
polymers by comparing intrinsic viscosities of capped and uncapped
polymers.

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* Previous reports are listed in Ref. 1.

Acetate-capped polymers are a good deal more stable than uncapped polymers, as expected. Surprisingly, however, capped polymers have been found subject to depolymerization under conditions tentatively identified with surface effects in certain types of infrared cells used for spectral studies. Some evidence for unidentified end groups other than acetate or hydroxyl in acetylated polymers has been observed.

Uncapped polymers undergo slow decomposition in the solid state during storage at temperatures of -20°C or lower. The primary effect occurring during storage is the formation of monomer, but another effect apparently is a reduction in molecular weight of polymer remaining. Uncapped polymers decompose in solution at room temperature with a rate that appears to depend on storage effects and on the type of solvent used. Observed depolymerization rates in solution were thus variable, ranging from 20% depolymerization in 23 hours by a freshly prepared polymer in chloroform to 100% depolymerization in 1 hour by an aged polymer in carbon tetrachloride. The rate of depolymerization may be faster in carbon tetrachloride than in chloroform because the ethanol preservative present in chloroform inhibits depolymerization. The increase in the rate of depolymerization in solution after prior storage may be due to catalytic effects by the accumulated monomeric impurity or to the reduction in molecular weight.

Since heptaldehyde polymers in the uncapped form degrade rapidly under certain conditions, they remain attractive for the proposed use in detection, insofar as the present information can reveal. The continuing problem in this investigation is to identify the specific causes of rapid depolymerization.

II. POLYMER SYNTHESIS AND STORAGE

This report presents information on six different heptaldehyde polymers - 3763-72, 3763-72A, 3763-97, 3763-121, 3763-121A, and 3763-130. The two designated with letter suffixes were fractions of original polymers that had been treated differently from the parent materials, as described later.

Two of the original polymers, 3763-72 and 3763-97, were recovered after an acetate capping procedure was carried out, as described in Ref. 1(d) and 1(e), respectively. These polymers have previously been termed "acetate-capped" polymers, and they are so designated in this report although they may contain end

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groups besides acetate. The polymer designated as 3763-72A was a fraction of 3763-72 that was recovered from carbon tetrachloride solutions used in vapor-pressure osmometry experiments for a molecular weight determination. This fraction has been used in further experiments because of the limited amount of the original material still available.

The other two original polymers, 3763-121 and 3763-130, were the products from recent syntheses carried out to obtain uncapped materials. The polymer designated as 3763-121A was a fraction of 3763-121 that was stored under different conditions. The heptaldehyde monomer used to prepare these polymers was Eastman Organic Chemicals No. 284, which was stored over $Na_2CO_3 \cdot H_2O$ (an alkaline drying agent) and distilled just before use. The distillation was carried out by adding 0.1% di-2-napthyl-p-phenylenediamine (an antioxidant) to the monomer, collecting the distillate at 56-58°C and 22 mm, and storing the distillate under nitrogen. Gas chromatographic analyses showed that unidentified impurities accounted for approximately 0.5% of the distillate collected.

In the syntheses of both 3763-121 and 3763-130, by the anionic polymerization method of Vogl,[2] 120 ml of hexane that had been dried over molecular sieves was added to a carefully dried, nitrogen-swept reaction vessel in a bath of dry ice and acetone. Next, 24 ml of 0.078 M potassium triphenylmethoxide in toluene was added as the catalyst; then, 20 ml of the monomer, which had been cooled to its freezing point (-42°C), was added. Each addition to the reaction vessel was made through serum stoppers by means of a hypodermic syringe. The cold mixture was stirred for 1 hour with a paddle-type stirrer, and then 100 ml of acetone containing 0.25% acetic acid was added to quench the polymerization by neutralizing alkoxide end groups in the polymer. The resulting mixture was further stirred for 5 minutes and then taken from the bath of dry ice and acetone and filtered while it was still cold. Then the polymer was washed with three 75-ml portions of acetone at room temperature, dried in a vacuum desiccator for about 1 hour, and stored. The amounts of polymers recovered were 10 and 11 g, corresponding to yields of 60 and 65%, respectively.

The conditions used for storing the polymers are summarized in Table I. The acetate-capped polymers have been stored at room temperature in loosely-capped vials since they were prepared. The procedure initially used with the uncapped polymers was to place a polymer in a sealed, nitrogen-filled container in contact with dry ice in an insulated chest. However, because of the danger of loss of refrigeration because of complete sublimation of the dry ice during week-end and holiday periods, the polymer samples

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Table I. Storage Conditions for Heptaldehyde Polymers

Number	Type	Conditions
3763-72	Acetate-capped	Prepared on 4/26/65 and subsequently stored at room temperature in air
3763-72A	Acetate-capped	Recovered from 3763-72 in CCl_4 solutions that were used in vapor-pressure osmometry experiments on 12/9/65 and stored subsequently at room temperature in air
3763-97	Acetate-capped	Prepared on 7/1/65 and subsequently stored at room temperature in air
3763-121	Uncapped	Prepared on 11/16/65 and then stored under N_2 in dry ice chest from 11/16/65 to 12/21/65 and then at -20°C since 12/21/65
3763-121A	Uncapped	Removed from 3763-121 on 11/30/65 and stored at -20°C under N_2 since that time
3763-130	Uncapped	Prepared on 12/7/65 and then stored under N_2 in dry ice chest from 12/7/65 to 12/21/65 and then at -20°C since 12/21/65

were later transferred to the freezing compartment of a refrig-
erator and kept under nitrogen at a temperature of approximately
-20°C. This temperature is near the estimated ceiling tempera-
ture of the polymers, at which spontaneous depolymerization is
possible.[2] However, it was expected that the kinetics of depoly-
merization at -20°C would be too slow to affect the polymer
appreciably, especially in the presence of a nitrogen atmosphere.

Samples of uncapped polymers were removed for study by
allowing the polymer to come rapidly to room temperature before
the sealed container was opened. Although the hazard of
promoting decomposition was thus introduced, this procedure
was followed to prevent water vapor from the air from condensing
on the polymer. After samples were removed, the container was
resealed, evacuated, filled with nitrogen, and again stored at
a low temperature.

III.   POLYMER CHARACTERIZATION STUDIES

This section deals principally with information obtained
to characterize polymers that had not undergone appreciable
decomposition. The following section (IV) presents related
information on polymers that had undergone decomposition under
storage conditions or under experimental conditions deliberately
imposed.

A.   Elemental Analyses

The theoretical carbon-hydrogen analysis of heptaldehyde
polymers, based on the monomer analysis, is C 73.66% and H 12.28%.
The results obtained for acetate-capped polymers - 3763-72, C 72.56%
and H 12.16%; 3763-97, C 73.23% and H 12.06% - were reasonably
satisfactory.

The results obtained for the uncapped polymers tended to be
low, especially after storage. For 3763-121, the results were C
72.91% and H 12.18% when the polymer was freshly prepared, and C
71.15% and H 11.37% when the polymer had been stored 45 days. For
3763-130, the results were C 71.31% and H 12.04%, when the first
analysis of the polymer was made after 23 days of storage.

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It is known that some heptaldehyde monomer was present in the uncapped polymers after storage, and the low results may be attributable to the monomer that was volatized with incomplete combustion during analyses. The results were lower the second time 3763-121 was analyzed, when it appeared to contain a fair amount of monomer.

An attempt was made to obtain more meaningful analyses of the uncapped polymers by analyzing their residues in a liquid form, obtained by pyrolyzing the polymers in a sealed, evacuated tube at 110°C for 2 days. The pyrolysis procedure extensively or completely converted the polymers to the monomer, and the residues were analyzed by a capillary procedure that is appropriate for volatile liquid samples. The analytical results, especially those for carbon, were unaccountably high: 3763-121, C 77.13% and H 12.42%; 3763-130, C 75.82% and H 12.38%.

B. Melting-Point Determinations

As stated in Ref. 1(d), a differential thermal analysis of one of the acetate-capped polymers, 3763-72, was performed with a Stone DTA apparatus with the sample under nitrogen. Small endothermal peaks observed at 80 and 90°C were attributed to a solid-phase transition, described by Vogl[2] as the "melting" of paraffinic side chains. A strong, broad peak centered at 165°C was attributed to the melting of the polymer, since Vogl reported melting at 150°C, and a broad endothermal effect above 165°C was attributed to thermal decomposition.

Since the polymer was not observed visually during the DTA experiment, a more or less conventional melting-point determination was made recently. A small amount of 3763-72 was placed in a Pyrex tube, and the tube was then evacuated and sealed. In the range 97-100°C, the solid changed to a cloudy liquid. The same melting range was observed for another fraction of this polymer, 3763-72A, and for the other acetate-capped polymer, 3763-97. However, the melting of an uncapped polymer, 3763-121, was observed at a lower range, 80-82°C. Perhaps the phenomena observed should be termed "liquefaction" rather than "melting", especially for the uncapped polymer since it most likely was partially decomposed when liquid was first observed.

It is believed that the difference in the melting characteristics of 3763-72 reported from DTA results and observed visually is due to an erroneous interpretation of the DTA results. The phenomenon responsible for the peak centered at 165°C actually began at approximately 110°C, a temperature not very different

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from the point of liquefaction observed visually. It thus
appears that the acetate-capped heptaldehyde polymers studied
in this program melt at a lower temperature, or are more liable
to undergo decomposition, than those described by Vogl.*

C.   Viscometry

Three different solvents - carbon tetrachloride, chloroform,
and tetrahydrofuran** - have thus far been used in experiments at
30°C that are designed to yield the intrinsic viscosities of
heptaldehyde polymers. Ubbelohde capillary viscometers have been
employed in these experiments.

The results previously available on the acetate-capped
polymers, 3763-72 and 3763-97, were summarized in Ref. 1(e).
These results indicated that the intrinsic viscosity, [n], for
3763-72 in tetrahydrofuran is 0.16. A reliable value of the
intrinsic viscosity for 3763-97 in tetrahydrofuran was not
obtained, since values of the reduced viscosity - $(n/n_0-1)/c'$,
where n/n_0 is the ratio of solution and solvent flow times and
c' is the polymer concentration in grams per deciliter - increased
as the concentration decreased. This is an anomalous behavior
that vitiates the interpretation of the intrinsic viscosity, which
is obtained by extrapolating the reduced viscosity to infinite
dilution. The same anomalous behavior was observed for 3763-72
in a different solvent - chloroform - and the results for this
polymer in the third solvent - carbon tetrachloride - were not
accurate enough for interpretation.

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* The polymers prepared in this program are also fairly soluble
  in nonpolar solvents, such as carbon tetrachloride, chloroform,
  and hexane, whereas those described by Vogl (Ref. 3) were not
  soluble. Polymers prepared by Novak and Whalley (Ref. 4) were
  soluble in carbon tetrachloride, however, and polymers prepared
  by Vogl, Novak and Whalley, and us were all crystalline, as
  discussed in Ref. 1(d).

** Reagent-grade solvents used in these and other experiments were:
  carbon tetrachloride, B & A Code 1554; chloroform, B & A, Code
  1564; and tetrahydrofuran, Fisher T-397. This chloroform
  contains 0.75% of ethanol as a preservative.

Further experiments at 30°C have now been conducted with the acetate-capped polymers in chloroform and carbon tetrachloride. In the first additional experiments, the polymers were studied in chloroform at concentrations of 0.5, 0.25, and 0.125 g/dl. Again, anomalous results were obtained, since the reduced viscosity value doubled or tripled in value as the concentration was reduced from 0.5 to 0.125. Subsequently, further experiments were done with both chloroform and carbon tetrachloride, but higher concentrations (4.0 to 0.5 g/dl) were used to improve the accuracy of the reduced viscosity values. Also, a further precaution - filtering the solutions through a medium-porosity, fritted-glass filter - was adopted. The results for 3763-72A in both solvents were thus substantially improved; this is shown by the results in Figure 1, which are considered reliable. The values indicated for the intrinsic viscosity for 3763-72A are 0.18 in carbon tetrachloride and 0.15 in chloroform and thus are near the value of 0.16 for 3763-72 in tetrahydrofuran that was determined earlier. The value indicated for 3763-97 in chloroform is 0.10, which indicates that the molecular weight of 3763-97 is relatively low.

Experiments at 30°C were also conducted with the uncapped polymers, 3763-121 and 3763-130, despite the possibility of difficulties from depolymerization of these relatively unstable polymers. In carbon tetrachloride solutions, 3763-121 yielded results that were very difficult to reproduce and that might very well have indicated decomposition. After 3763-121 had been in carbon tetrachloride for 2 hours at 30°C, its viscosity at a concentration of 0.5 g/dl was lower by 50%. However, 3763-121 yielded identical results in chloroform and tetrahydrofuran at 30°C and appeared to be relatively stable, as did 3763-130 in chloroform. The results shown by lines (1) and (2) in Figure 2 for chloroform solutions* were obtained by beginning with the most concentrated polymer solution in the viscometer, making successive dilutions, and obtaining flow times in triplicate at each concentration. This procedure required from 30 minutes to 1 hour, and the absence of any large downward trend in the reduced viscosity values signified that no appreciable depolymerization occurred. Moreover, the reduced viscosity of 3763-121 in tetrahydrofuran after 2 hours at 30°C was unchanged.

Values of intrinsic viscosity of the uncapped polymers were as follows: 3763-121, 0.11 in either chloroform or tetrahydrofuran; 3763-130, 0.13 in chloroform. The molecular weights of these uncapped polymers thus appeared to lie between those of the two acetate-capped polymers evaluated.

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* Results shown by line (3) were for a polymer partially degraded in storage and are discussed later.

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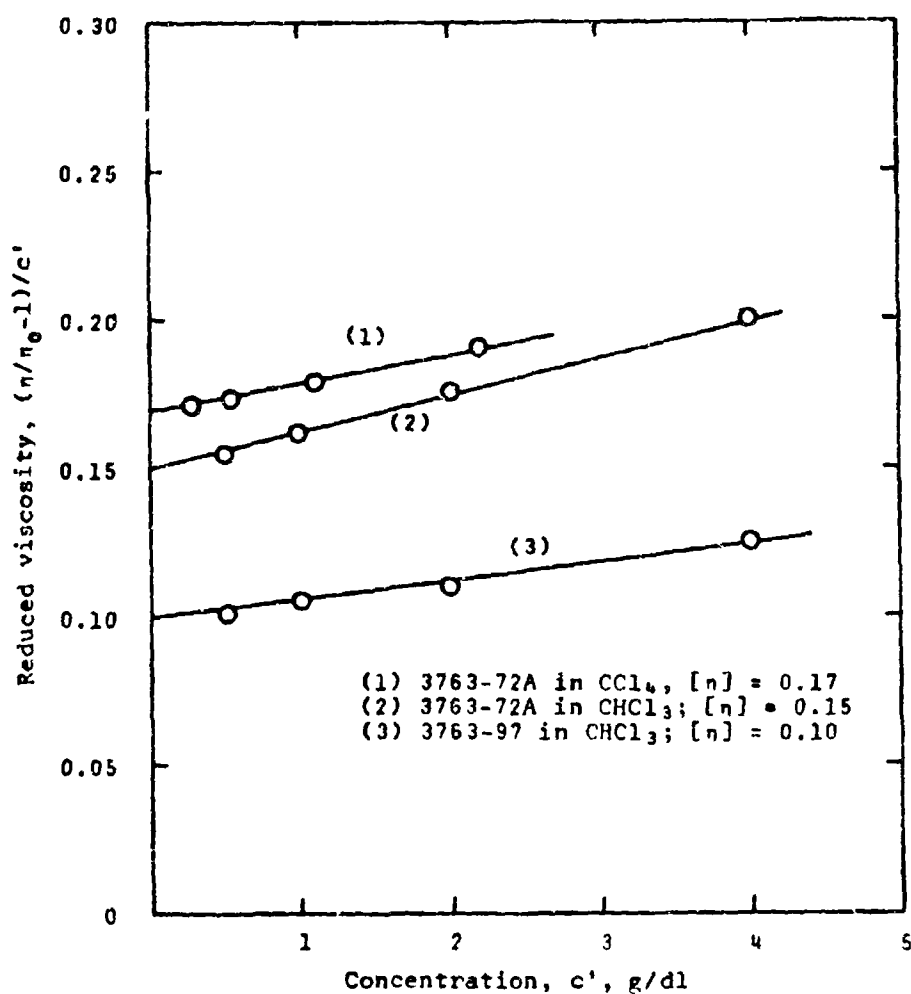
Figure 1. Viscosity Data for Acetate-Capped Polymers in Chloroform and Carbon Tetrachloride at 30°C

The figure plots Reduced viscosity, $(\eta/\eta_0 - 1)/c'$ versus Concentration, c', g/dl.

(1) 3763-72A in CCl_4, $[\eta] = 0.17$
(2) 3763-72A in $CHCl_3$; $[\eta] = 0.15$
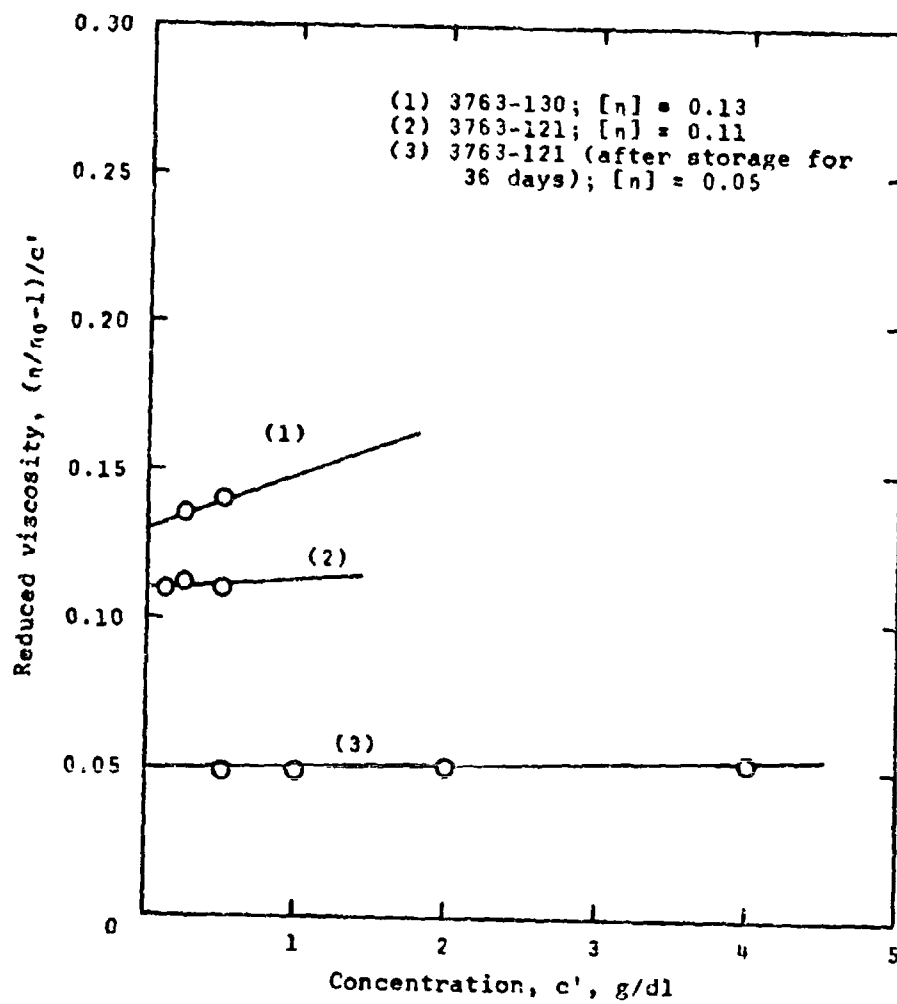(3) 3763-97 in $CHCl_3$; $[\eta] = 0.10$

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Figure 2. Viscosity Data for Uncapped Polymers in Chloroform at 30°C

Little comparative information has been found in the literature on the solution viscosities of aldehyde polymers. Weissermel and Schmieder[5] reported data for acetaldehyde polymers in 2-butanone, but the heptaldehyde polymers investigated in this program are not soluble in this solvent. Brame et al.[6] reported inherent viscosities* of 2.6-2.7 for acetaldehyde polymers of "high molecular weight" in 2-butanone at 0.1 g/dl and an unspecified temperature, and inherent viscosities of 0.33-0.42 for these polymers of "moderate molecular weight" in 2-butanone and in tetrachlorethylene at 0.5 g/dl and 20°C. If compared with the acetaldehyde polymers of Brame et al., the heptaldehyde polymers studied in this program would appear to have relatively low molecular weights.

D.   Vapor-Pressure Osmometry

Light-scattering experiments to determine the absolute weight-average molecular weight of one of the acetate-capped polymers, 3763-72, yielded decidedly conflicting results, as discussed in Ref. 1(e). Recently, vapor-pressure osmometry was employed as a method for determining the number-average molecular weight of this polymer. The instrument used was Osmometer Model 302 of Mechrolab, Inc. Measurements were made at 37°C with carbon tetrachloride solutions at concentrations less than 7% (w/v). The results indicate that the number-average molecular weight is 5,200, which corresponds to an average degree of polymerization of 45.

It is believed that the actual molecular weight is perhaps greater than 5,200. Molecular-weight determinations from colligative properties, such as vapor pressure, are very sensitive to impurities of low molecular weights. For example, a monomer impurity of 1% by weight in a polymer with an average degree of polymerization of 100 would cause the apparent degree of polymerization to be only 50. Since unidentified impurities might have been present at the 1% level, the number-average molecular weight for 3763-72 might be nearer 10,000 than 5,000.

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* Inherent viscosity is defined as the quantity $(\ln \eta/\eta_0)/c'$. If the inherent viscosity at $c' = 0.1$ g/dl is 2.6-2.7, the reduced viscosity is approximately 3.0. If the inherent viscosity at $c' = 0.5$ g/dl is 0.33-0.42, the reduced viscosity is 0.36-0.47.

A number-average molecular weight for 3763-72 in the range
of 5,000-10,000 is consistent with a weight-average value of
16,000 but not 300,000. These are the values given in Ref. 1(e)
as a result of light-scattering experiments with carbon disulfide
and tetrahydrofuran solutions, respectively.

E.   Nuclear Magnetic Resonance Spectrometry

A nuclear magnetic resonance (n.m.r.) spectrum of one of the
acetate-capped polymers, 3763-97, is shown in Figure 3. This
spectrum was obtained with a Varian A-60 spectrometer with a 10%
(w/v) solution of the polymer in carbon tetrachloride at a tempera-
ture of 34°C.

In this spectrum, there are peaks identifiable with only
three types of proton groups, all of which are present in the
structure of polyheptaldehyde: $-CH_3$, $-CH_2-$, and $>CH-O-$. The
respective peaks are at 0.9, 1.4, and 4.8 ppm downfield from
internal tetramethylsilane (TMS). Positions assigned to $-CH_3$
and $>CH-O-$ protons are consistent with positions assigned by
Brame et al. to those types of protons in polyacetaldehyde.[6]
The observed ratio of $>CH-O-$ protons to $-CH_3$ plus $-CH_2-$ protons
is 1:13, which is the theoretical value.

An n.m.r. spectrum of one of the uncapped polymers, 3763-121,
at a concentration of 10% (w/v) in carbon tetrachloride is also
shown in Figure 4. This spectrum was recorded with a Varian A-60A
spectrometer, which has replaced the older A-60. This spectrum
covers a narrower range, but the only significant difference from
the spectrum discussed above is a peak at 2.3 ppm that is due to
α -CH_2- protons of heptaldehyde monomeric impurity in 3763-121.
The presence of this depolymerization product in the relatively
unstable uncapped polymer was not surprising, since the temperature
of the sample was 38°C. After the spectrum shown in Figure 4 was
recorded, the polymer solution was heated at 50°C for 1 hour and
then the spectrum of the residue from the polymer was recorded.
It was identical with the spectrum of heptaldehyde monomer, as
shown by peaks for four types of protons: $-CH_3$; two types of
$-CH_2-$, those in the α position being distinguishable from the
others; and $-CH=O$. The position of the $-CH=O$ peak is 9.6 ppm;
therefore, this peak did not appear in the 8.0-ppm range shown
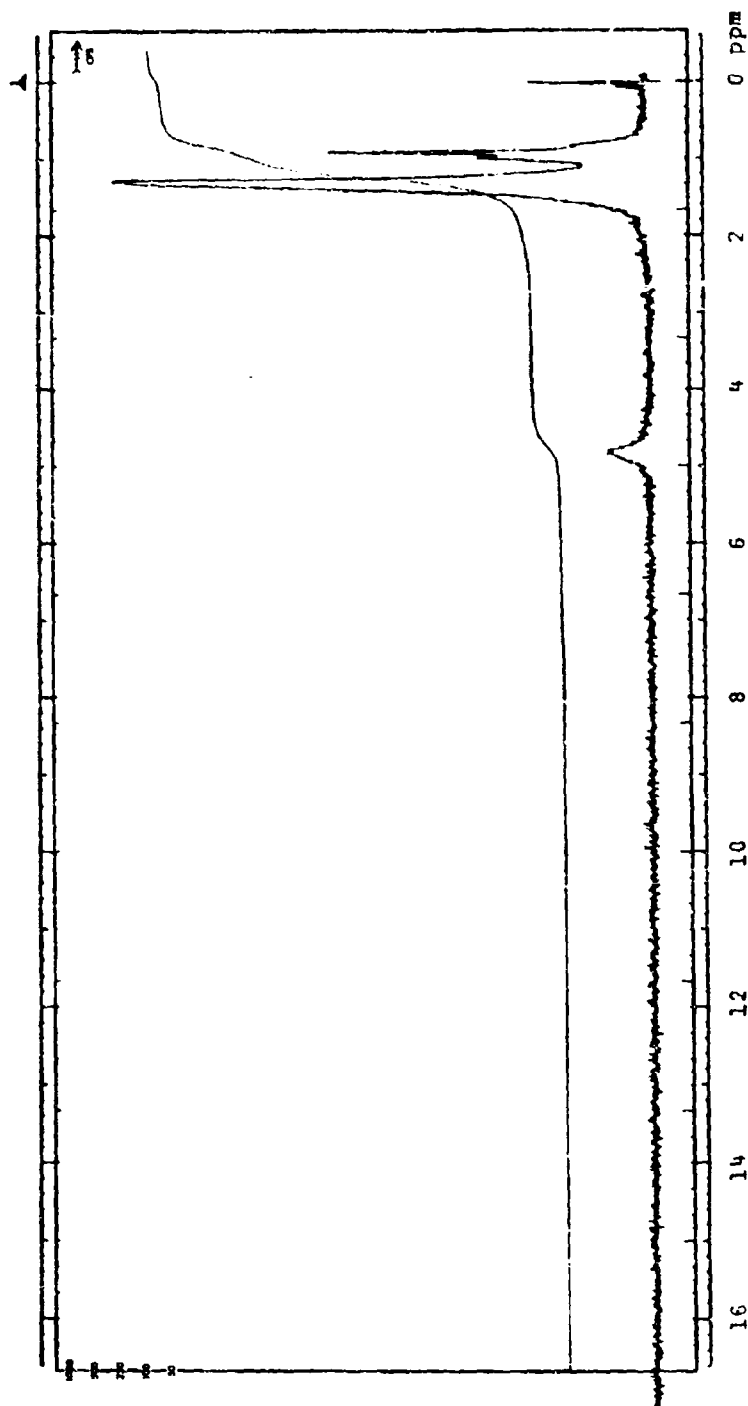in Figure 4, whereas the α -CH_2- peak did appear.

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Figure 3. N.m.r. Spectrum of an Acetate-Capped
Heptaldehyde Polymer (3763-97) in Carbon Tetrachloride
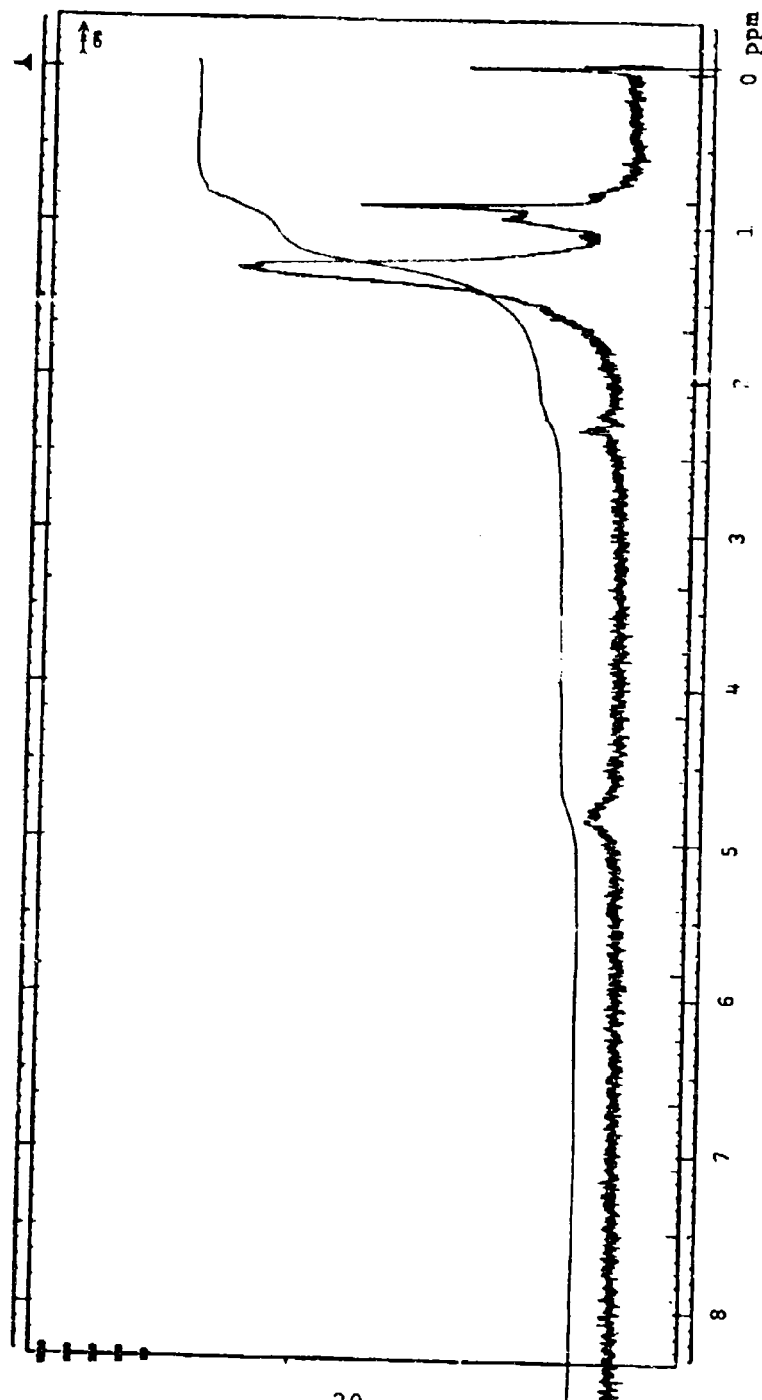
Figure 4. N.m.r. Spectrum of an Uncapped
Heptaldehyde Polymer (3763-121) in Carbon Tetrachloride

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F.   Infrared Spectrometry

The infrared spectra of various polymers have been recorded with Perkin-Elmer 221-G and 521 spectrometers, usually with the polymer dissolved in carbon tetrachloride but occasionally in chloroform or tetrahydrofuran. Tetrahydrofuran is not usually desirable because its spectrum has ether-linkage absorption bands that obscure the ether-linkage bands of the polymer, and it has a limited solvent action toward heptaldehyde polymers. The infrared spectra of polymers have also been recorded with films obtained by pressing the polymer at room temperature at a pressure of 2000 psi or less. Features barely evident in solution spectra are clearly seen in the spectra of films.

1.   Polymer 3763-72

An infrared spectrum of this acetate-capped polymer at a concentration of 5% (w/v) in carbon tetrachloride was presented in Ref. 1(d). In this spectrum, there was a strong absorption band at 1100 cm^{-1}, which is characteristic of all heptaldehyde polymers studied and is attributable to the stretching of C-O bonds in the polymer backbone. A spectrum of a pressed film of this polymer, approximately 150 microns thick, is presented in Figure 5(a). The principal features of this spectrum that are of interest are as follows:

(1) There is no absorption near 3400 cm^{-1}, which should be present only if any hydroxyl end groups of the polymer were not acetylated.

(2) There is a band at 1740 cm^{-1}, which is attributable to carbonyl bonds in ester end groups formed by acetylation.

(3) There is an unassigned band at 1660 cm^{-1}, which is even stronger than the one at 1740 cm^{-1}. Possible assignments of the 1660-cm^{-1} band are discussed later.

2.   Polymer 3763-97

The spectrum of this acetate-capped polymer in carbon tetrachloride was barely distinguishable from that of the other acetate-capped polymer, 3763-72. However, the spectrum in Figure 5(b) for a film of 3763-97, estimated to be between 150 and 200 microns thick, has important differences from the spectrum of a film of 3763-72 in Figure 5(a). In the spectrum of 3763-97, the 1740-cm^{-1} band is relatively weak and the 1660-cm^{-1} band is relatively strong.
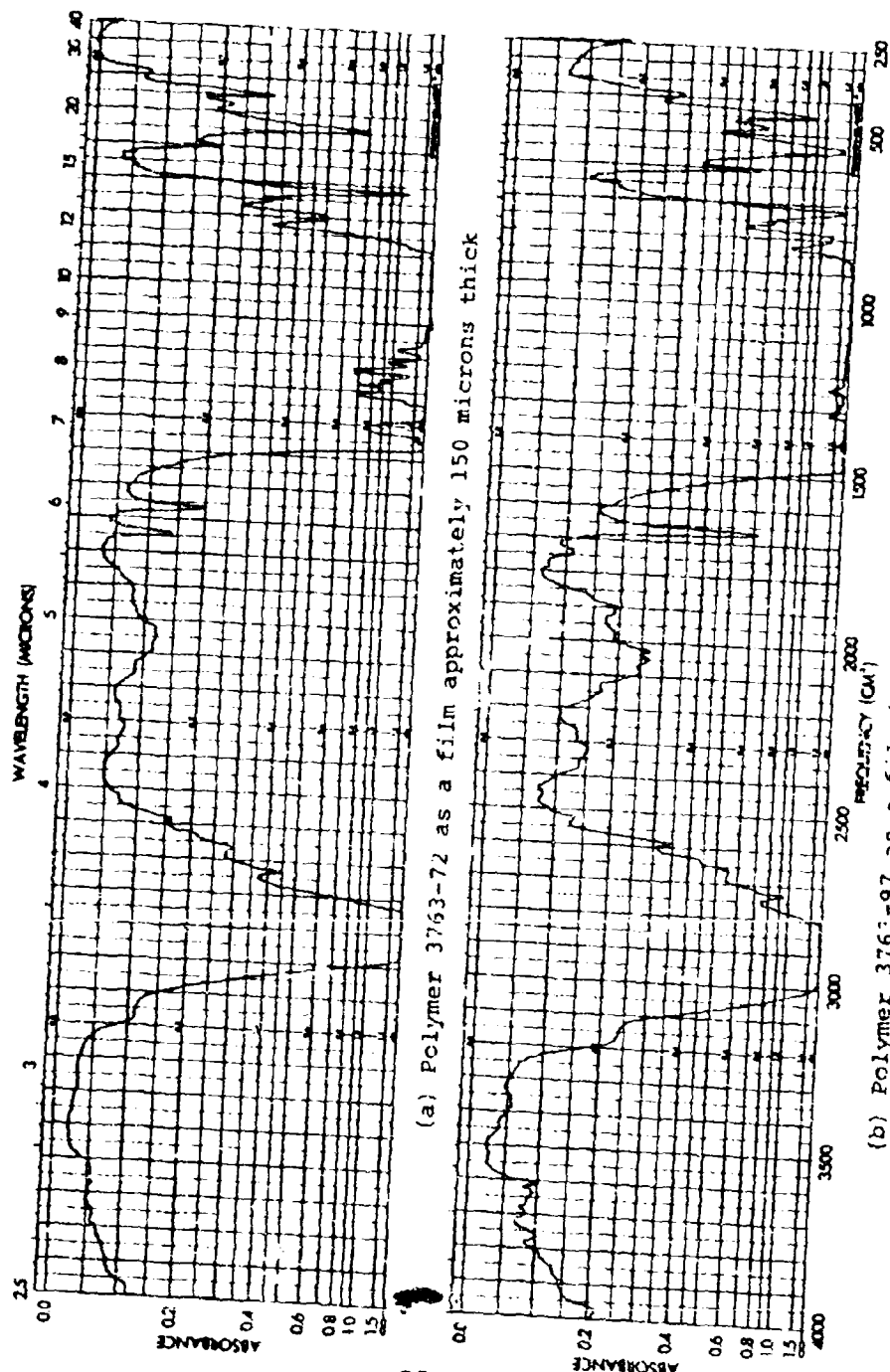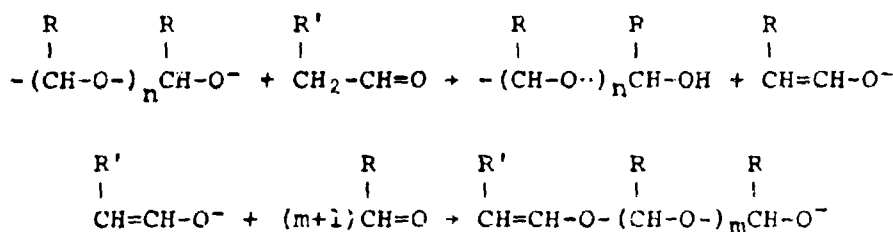
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(a) Polymer 3763-72 as a film approximately 150 microns thick

(b) Polymer 3763-97 as a film between 150 and 200 microns thick

Figure 5. Infrared Absorption Spectra of Acetate-Capped Heptaldehyde Polymers

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If the 1740-cm^{-1} band were caused by acetate end groups in both polymers, as seems likely, and the molecular weight of 3763-97 were less than that of 3763-72, as viscosity data indicate, it would then appear that end groups of a type not now identified are present in 3763-97 and, to a lesser extent, in 3763-72. These end groups may very well be responsible for the unassigned 1660-cm^{-1} band, since the end groups not identified evidently are not unacetylated hydroxyl groups.

It is possible that the 1660-cm^{-1} band is caused by carbon-carbon double bonds, which might be present in the polymer in end groups with the structure $CH_3(CH_2)_4CH{=}CH{-}O{-}$. Groups of this type might be formed during polymerization, as described by Vogl and Bryant,[7] by the transfer of a proton from a monomer molecule to a polymer chain and by the subsequent polymerization onto the proton-deficient monomer unit:

$$-(\underset{\underset{R}{|}}{CH}{-}O{-})_n\underset{\underset{R}{|}}{CH}{-}O^- + CH_2{-}\underset{\underset{R'}{|}}{CH}{=}O \rightarrow -(\underset{\underset{R}{|}}{CH}{-}O{\cdots})_n\underset{\underset{R}{|}}{CH}{-}OH + \underset{\underset{R}{|}}{CH}{=}CH{-}O^-$$

$$\underset{\underset{R'}{|}}{CH}{=}CH{-}O^- + (m{+}1)\underset{\underset{R}{|}}{CH}{=}O \rightarrow \underset{\underset{R'}{|}}{CH}{=}CH{-}O{-}(\underset{\underset{R}{|}}{CH}{-}O{-})_m\underset{\underset{R}{|}}{CH}{-}O^-$$

where $R = CH_3(CH_2)_5$ and $R' = CH_3(CH_2)_4$

The assignment of the 1660-cm^{-1} band to carbon-carbon double bonds seems unreasonable, however, since this band has been seen only in the spectra of acetate-capped polymers. Moreover, since carbon-carbon double bonds have weak absorptions[8] the molecular weight of 3763-72 estimated from the infrared spectrum by assuming unsaturated end groups were present was nearer a value of 500 than the value of 5,200 indicated by vapor-pressure osmometry.

Various types of relatively uncommon carbonyl groups absorb near 1660 cm^{-1}. None of these groups listed by Bellamy,[8] however, seems likely in the polymers prepared.

3.   Polymer 3763-121

      The spectrum of a 150-micron film of this uncapped
polymer, shown in Figure 6(a), differs from the spectra of
films of acetate-capped polymers. It has a very strong broad
absorption band near 3400 cm^{-1}, which is presumably caused by
hydroxyl end groups; it also has a band in the carbonyl region
that is located at 1730 cm^{-1} rather than 1740 cm^{-1}. It is
believed that the 10 cm^{-1} difference in band positions in the
carbonyl region is significant and is caused by different types
of carbonyl groups. The absorption at 1730 cm^{-1} by the uncapped
polymer is believed to be caused by heptaldehyde monomeric impurity,
and the absorption at 1740 cm^{-1} by the capped polymers is attri-
buted to acetate end groups.

      The spectrum of 3763-121 at a concentration of 5% (w/v)
in carbon tetrachloride is shown in Figure 6(b). The band at
1100 cm^{-1}, which cannot be seen in the spectrum of the film owing
to the opaqueness of the film in this spectral region, is caused
by the characteristic ether linkage of the polymer backbone.
Absorptions at 1730 cm^{-1} (assigned to a monomeric impurity) and
near 3400 cm^{-1} (assigned to hydroxyl end groups) are evident in
the solution spectrum as well as in the film spectrum.

      The spectra presented for 3763-121 were obtained when the
polymer was freshly prepared. The solution spectrum was recorded
within 30 minutes after the polymer was dissolved; however, as
discussed later, it changed rapidly as the polymer remained in
solution.

IV.   DEPOLYMERIZATION STUDIES

      Much of the information here is based on adventitious
observations rather than results from planned kinetic experiments.
As this information shows, the results from planned experiments
were complicated by changes in the behavior of uncapped polymers
after increasing times of storage. Some of the observations
presented here are given tentative interpretations and are
subject to reinterpretation later.

A.   Acetate-Capped Polymers

1.   In solid state

      Acetate-capped polymers are much more stable than uncapped
polymers, and they have not apparently undergone decomposition
during storage at room temperature in air in periods of 6 to 8
months.

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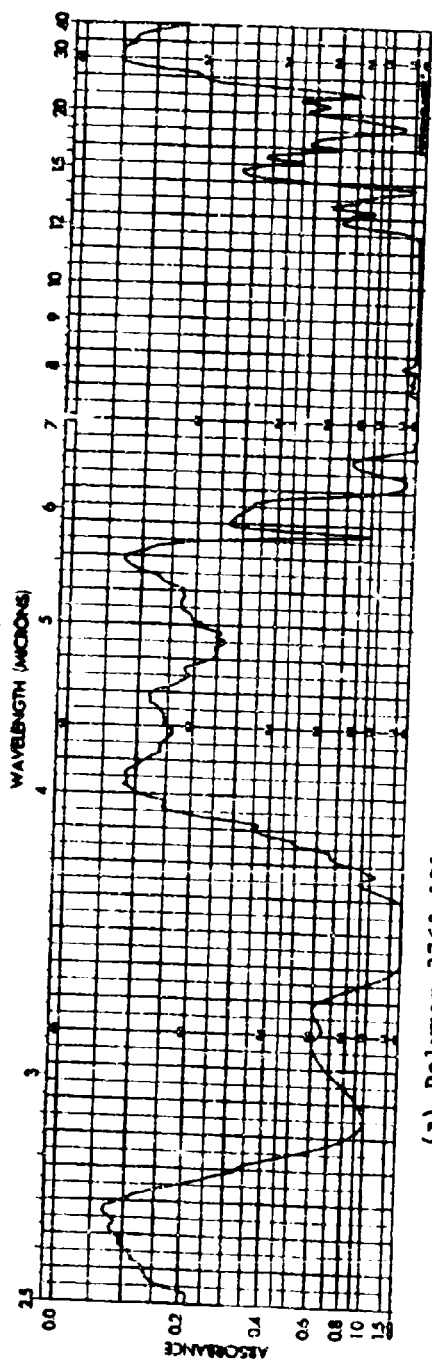
(a) Polymer 3763-121 as a film approximately 150 microns thick
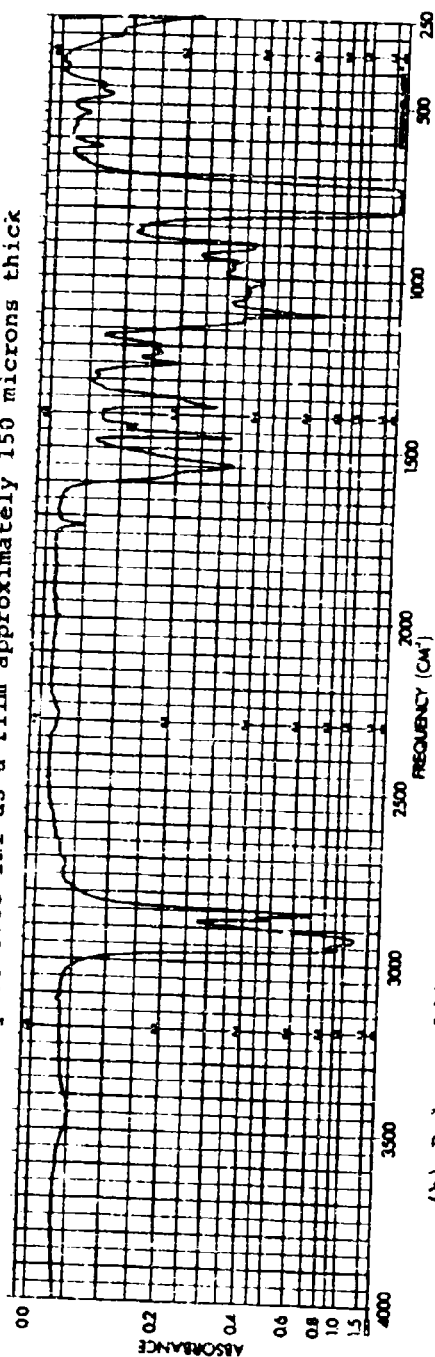
(b) Polymer 3763-121 at 5% (w/v) in carbon tetrachloride in a 0.1-mm cell

Figure 6. Infrared Absorption Spectra of an Uncapped Heptaldehyde Polymer

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2. In liquid state

A sample of 3763-97 was sealed in a Pyrex tube under a vacuum and then left in an oven at 110°C (approximately 10°C above the melting point) for a total of 45 hours. While cooling, the sample changed from a viscous liquid to a gel-like substance, which was probably a mixture of polymer and monomer formed by partial depolymerization. During the cooling period, a vapor (undoubtedly monomer) condensed on the walls of the tube. All of the material in the tube was dissolved in carbon tetrachloride and analyzed by infrared spectrometry and gas chromatography. A comparison of the intensities of monomer and polymer absorption bands at 1730 and 1100 cm^{-1}, respectively, with the intensities of these bands for pure monomer and polymer in solution showed that 70-75% of the sample still remained in the polymeric form; no other substance besides monomer and polymer was recognized from the infrared spectrum. The gas chromatographic analysis showed that several volatile components besides monomer were present, but the total amount of these unidentified components was not more than 0.3% of the amount of monomer.

These results show that only part of the polymer decomposed at the elevated temperature. It is not known presently whether part of the polymer was more stable than the rest or the rate of the polymerization was too slow to decompose all of the sample in 45 hours. There is infrared evidence that there may be another type of end group besides acetate in this polymer; if so, the fraction decomposed during heating might have been that with the unidentified end groups.

3. In solution

The acetate-capped polymers do not appear to undergo detectable decomposition during 10 days in a carbon tetrachloride solution contained by Pyrex glassware at room temperature in the presence of air and normal illumination.

One polymer, 3763-72, underwent no detectable decomposition at a concentration of 5% (w/v) during 4 hours in a carbon tetrachloride solution that contained 0.3% (w/v) heptanoic acid, a probable decomposition catalyst if its concentration is high enough. No detectable decomposition of this polymer was observed at a concentration of 2.5% (w/v) during a longer period, 18 hours, in a water-saturated carbon tetrachloride solution that contained

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0.15% (w/v) heptanoic acid. These observations, which were described in Ref. 1(e), were made by keeping the solutions in a 0.1-mm infrared cell (equipped with sodium chloride windows sealed by means of an amalgamated lead spacer*) throughout the periods of time stated and by periodically inserting the cell in the spectrometer and scanning the spectra.

Quite surprisingly, however, acetate-capped polymers appear subject to depolymerization when they are kept in certain types of infrared cells without acid present. The first observation of this phenomenon was made with solutions of 3763-97. In a 0.1-mm fixed-thickness, sodium chloride cell, the polymer was 75% depolymerized after 24 hours.** In a similar cell, except for windows of cesium bromide, the polymer was 10% depolymerized after 7 hours and 75% depolymerized after 72 hours when the second spectral scan was made. On the contrary, in a 0.1-mm cavity cell of sodium chloride - a cell consisting of a hole drilled in a block of salt, with no lead spacer - not more than 5% of the polymer depolymerized in 72 hours. Also, the polymer decomposed less slowly in a 1.0-mm fixed-thickness, cesium bromide cell than in a 0.1-mm cell of the same type.

The other capped polymer, 3763-72, also underwent decomposition in an acid-free solution of carbon tetrachloride that was kept in a 0.1-mm fixed-thickness, cesium bromide cell. After 7 hours, 1-2% had depolymerized; after 24 hours, approximately 50% had decomposed. The rate of depolymerization of this polymer apparently was slower than that of 3763-97 in the same infrared cell. The remarkable aspect of these results with 3763-72, in contrast to earlier results, is this: the polymer appeared to be stable with acid present but unstable with acid absent, despite the catalytic effect that acids have on polyaldehyde decomposition.[9]

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* This type of cell is later called simply a "fixed-thickness, sodium chloride cell," and the same type with cesium bromide windows is designated in an analogous way.

** This estimate was based on a calculation of the monomer concentration from the intensity of the 1730-cm^{-1} band observed. Another estimate, based on a calculation of the residual polymer concentration from the intensity of the 1100-cm^{-1} band, was the same, considering the inaccuracy resulting from the small difference between polymer and solvent absorptions at that position.

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The best interpretation at present for the observations cited above is that lead surfaces in infrared cells, or perhaps the lead-amalgam cement used between the lead spacers and the salt windows, catalyze a type of decomposition that is inhibited by dilute acid. The decomposition seems not to be caused, in a primary sense, by either sodium chloride or cesium bromide surfaces or by mild heating effects produced by infrared radiation during the intermittent spectral scans. The structural component of the polymers that renders decomposition possible may be end groups that conceivably are responsible for the unassigned infrared bands at 1660 cm^{-1}. This possibility is suggested since 3763-97 has a stronger absorption at this frequency than 3763-72, and it also has a greater tendency to depolymerize. The 1660-cm^{-1} band seems to disappear as depolymerization becomes extensive. However, this observation is not clear-cut, since the band is weak to begin with and tends to be obscured by the intense monomer band that appears at 1730 cm^{-1}.

B.   Uncapped Polymers

1.   In solid state

The decomposition of uncapped polymers in the solid state occurred slowly even at the low temperatures used for storage. Clear evidence for this was encountered with 3763-130, which was kept in a container under nitrogen at the temperature of dry ice for 14 days and then at -20°C for 8 days and subjected to decomposition during sampling only once during this period. The odor of heptaldehyde monomer from the sample after 22 days was very strong. An attempt was made to estimate the percentage of monomer in the sample after storage by the infrared analysis of a carbon tetrachloride solution. However, the results of this analysis, which are presented later, indicated that depolymerization in the solution was too fast to permit a reliable estimate of the monomer percentage before solvent was added.

The decomposition of another uncapped polymer, 3763-121, during storage in the solid state was noted from the increased monomer odor. Viscosity properties and infrared spectra in solution also gave evidence of depolymerization. After 3 days of storage, the intrinsic viscosity in chloroform was 0.11, shown previously in Figure 2; after 36 days, the value was only 0.05, also shown in Figure 2. One explanation for the decrease in the intrinsic viscosity was the presence of a high percentage of monomer in the sample; in other words, the concentrations used to evaluate the intrinsic viscosity were not the residual

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polymer concentrations but the sum of polymer and monomer concen-
trations. Another probable explanation was a decrease in the
average molecular weight of the polymer remaining during storage.
If the molecular weight had not decreased, the comparison of
intrinsic viscosities would indicate that 55% of the sample existed
as monomer after 36 days.

The infrared data for polymer solutions in Table II show
that the amount of monomer increased as the storage time increased.
The values listed in the fifth column of this table, with one
exception, are considered fairly reliable estimates of the per-
centage of monomer present after storage but before solvent addition.
The value of 45% on the third line might be high, since it could
include monomer formed in solution. Even at the 45% level, the
amount of monomer was less than the amount that had to be present
to account for the previously cited viscosity change in terms only
of conversion to monomer. Part of the viscosity change is thus
attributed to a reduction in molecular weight.

After 44 days of storage, two samples of 3763-121, which
contained a good deal of monomer as shown by the evidence in
Table II, were observed to undergo fairly rapid decomposition in
the solid state at room temperature.* One sample was left in a
vial sealed with a serum cap; the other was left in an open
vial. Within 1 hour, a marked change had occurred in the
appearance of each. The particles had lost their white, crystalline
appearance and become gel-like in appearance. After 2.5 hours, both
samples contained a considerable amount of liquid; and after 22
hours, both were mostly in a liquid form. The percentages of the
initial weight of the sample in the open vial decreased with time
as monomer evaporated; the results were as follows: 1 hour, 96%;
2.5 hours, 90%; 4.5 hours, 85%; 22 hours, 78%. Infrared spectra
of the residues showed that both were mostly carboxylic acid,
assumed to be heptanoic acid formed by air oxidation of heptaldehyde.
Undoubtedly, the samples contained a high proportion of heptanoic
acid in the liquid phase throughout the period of decomposition,
and the acid played an important role in the decomposition.

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* Since heptaldehyde polymers have a limited solubility in the
  monomer at room temperature, they appeared to decompose as
  solids in the presence of a liquid monomer phase.

Table II. Monomeric Impurities in Uncapped Polymers After Storage

Polymer	Time in storage, days[a]	Solvent added	Time in solution, hr[b]	Monomer present, %[c]	Conversion rate to monomer, %/hr[d]
3763-121	3	CCl_4	0.5	3	5
3763-121	16	$CHCl_3$	0.5	7	1
3763-121	36	$CHCl_3$	0.25	45	–
3763-121A	36	$CHCl_3$	0.25	15	3

[a] Storage conditions are summarized in Table I.

[b] Before the first scan of the spectrum.

[c] At the time of the first scan. The values are based on a comparison of the intensity of the 1730-cm^{-1} band in the polymer spectrum with the intensity of this band in the monomer spectrum. Each value, except that on the third line, is assumed to be an approximate measure of the monomer present before solvent was added, since estimates of the rate of conversion to monomer in solution were not very high.

[d] In solution, based on later scans.

2.   In liquid state

Samples of 3763-121 and 3763-130 were sealed in Pyrex
tubes under a vacuum and heated as liquids at 110°C for 2 days.
After cooling, they remained as liquids and probably were
completely depolymerized. They were thus unlike one of the
capped polymers treated under the same conditions (Section IV-A-2).
No analyses of the residues were carried out, except the carbon-
hydrogen analyses previously cited (Section III-A). In further
similar experiments, it will obviously be desirable to analyze
the residues by infrared spectrometry and gas chromatography,
particularly since the results of carbon-hydrogen analyses were
anomalous.

3.   In solution

a. Polymer 3763-121*

The first observations on the depolymerization of 3763-121
in solution at room temperature were made when the polymer was
freshly prepared (stored only 3 days). A carbon tetrachloride
solution was prepared to contain the polymer at a concentration
of 5% (w/v), and the solution was placed in a 0.1-mm fixed-thickness,
cesium bromide cell and allowed to remain in the cell for periodic
scans. Approximately 30 minutes after the solvent was added to
the polymer, the cell was placed in the spectrometer, and the
spectrum was scanned. A comparison of monomer and polymer absorption
bands at 1730 and 1100 cm^{-1} indicated that 3% of the sample existed
in the monomeric form. Subsequent spectral scans that were made
by placing the cell in the spectrometer again only for the duration
of the scanning time indicated that 10-15% of the sample was monomeric
after 2.5 hours and 100% was monomeric after 22 hours.

The depolymerization rate of the polymer in carbon tetrachloride
after a longer storage time was markedly faster than originally
observed, and it was also markedly faster in carbon tetrachloride
than in chloroform or tetrahydrofuran. After 16 days of storage, the
polymer was dissolved under nitrogen in carbon tetrachloride,
chloroform, and tetrahydrofuran at concentrations of 2.5, 2.5, and

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* In addition to the information given here, see also the results
  in Section III-D on n.m.r. spectra.

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0.5% (w/v), respectively,* and kept at room temperature in bottles sealed with silicone stoppers. Periodically, a sample was removed from each bottle with a hypodermic syringe and placed in an infrared cell for a spectral scan. Owing to the fact that rapid depolymerization was not expected in any of the solutions, the scans of the spectra were not repeated for the carbon tetrachloride solution as frequently as later found desirable. The first scan, approximately 30 minutes after carbon tetrachloride was added to the polymer, indicated that 7% was present in the monomeric form; the second scan 3.5 hours later indicated that 95-100% was monomeric. In chloroform, on the other hand, only about 20% was monomeric after 23 hours; and in tetrahydrofuran, the increase in the proportion of monomer was barely detectable after 23 hours.

A possible cause for the difference in depolymerization rates in carbon tetrachloride and chloroform was the presence of ethanol (0.75%) in chloroform as a preservative. If the mechanism of depolymerization is an end-initiated chain process involving anionic end groups (the reverse of the polymerization mechanism[7]),

$$-(CH-O-)_n CH-O^- \rightarrow -(CH-O-)_{n-1} CH-O^- + CH=O$$

(with R substituents shown on each CH carbon)
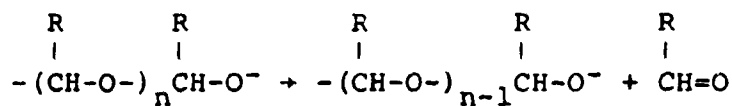
ethanol might inhibit the process by providing protons to neutralize anionic end groups. To test this hypothesis, a comparison was made between the depolymerization rates of 3763-121 in CCl$_4$ with ethanol absent and with 0.75% of ethanol added. Since a rapid depolymerization was expected with ethanol absent, the comparison was made by keeping both solutions in a 0.1-mm fixed-thickness cell in the infrared beam and making frequent repetitive scans. The results obtained, shown in Figure 7, appeared to indicate an initial faster depolymerization with ethanol present than with an ethanol absent, contrary to the expectation. However, a conservative appraisal of the results, based on the solid lines shown, is that ethanol had little effect on the rate in carbon tetrachloride, since the slopes of the two lines do not differ.

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* The polymer had a limited solubility in tetrahydrofuran; hence the concentration used in this solvent was relatively low. The 1100 cm^{-1} absorption band of the polymer was obscured by the solvent absorption, and only the absorption at 1730 cm^{-1} by the monomer was detectable.
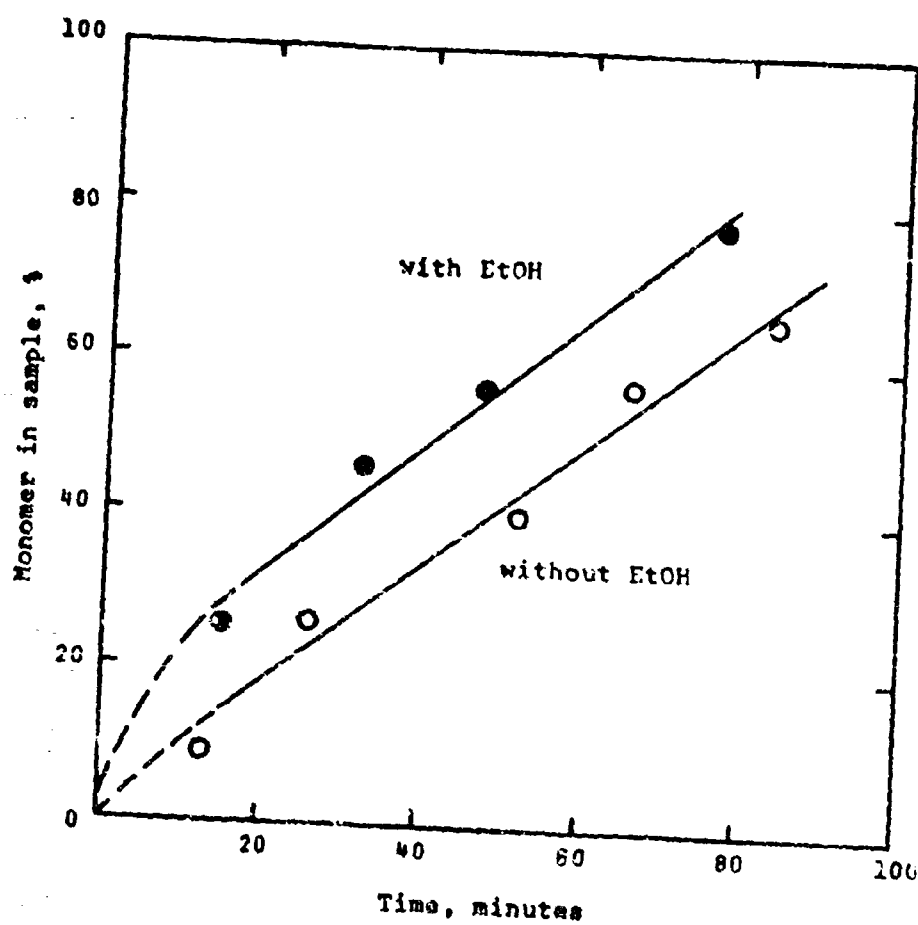
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Figure 7. Conversion of Uncapped Heptaldehyde Polymer
to Monomer in Carbon Tetrachloride with and
without Ethanol Added

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A later experiment with a different fraction of the same polymer, 3763-121A, was conducted after 36 days of storage. The infrared spectrum recorded 15 minutes after chloroform was added to dissolve the polymer showed that approximately 15% of the sample was monomeric; finally, after 27 hours, the sample was entirely depolymerized. In a previous experiment, with 3763-121 after only 16 days of storage, 80% remained polymeric after 22 hours in chloroform.

b. Polymer 3763-130

No attempt was made to observe the depolymerization rate of this polymer immediately after it was prepared. However, after it had been stored for 22 days (and obviously had increased in monomer content, as stated on page 28), a sample was dissolved at a concentration of 2% (w/v) in carbon tetrachloride and the spectrum was scanned in two infrared regions, 1900-1600 cm^{-1} and 1200-1000 cm^{-1}. Because a trace of insoluble matter was present, it was necessary to filter the solution before scanning its spectrum; thus, a longer time than desired, approximately 35 minutes, elapsed between the solvent addition and the first spectral scan. Based on intensities of the monomer band at 1730 cm^{-1} and the polymer band at 1100 cm^{-1}, the fraction of the sample existing as monomer was 50% after 35 minutes and 100% after 60 minutes, when the second scan was made. (Samples of the solution were transferred to the cell from a bottle for each scan.)

In an experiment conducted concurrently, enough heptaldehyde monomer was added to the previous solution, 30 minutes after the solvent was initially added, to make the monomer concentration 2% (w/v), over and above that formed by the polymer decomposition. A scan of the resulting solution with added monomer showed that none of the polymer remained 45 minutes after solvent was first added, whereas without added monomer about 50% remained 35 minutes after solvent was added. The added monomer appeared to accelerate the decomposition. However, this conclusion is not definite, because the rate of depolymerization was rapid with or without monomer added.

In another experiment conducted concurrently, heptanoic acid was added to the original polymer solution in order to determine the effect of acid. By the time the acid was added and the spectrum was recorded, no residual polymer was present. However, by this time, none was present even with acid absent; thus, no conclusion was drawn from this experiment about the influence of acid on the depolymerization rate.

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V. CONCLUSIONS AND PLANS FOR FUTURE WORK

Various kinds of information presented in this report show convincingly that linear polyacetals have been obtained by polymerizing heptaldehyde. This conclusion is based especially on the infrared and n.m.r. spectral properties of both the polymers synthesized and the monomeric residues obtained by degrading the polymers. It is also supported by determinations of intrinsic viscosity and molecular weight.

Acetate-capped polymers are much more stable than uncapped polymers under most of the conditions investigated. The depolymerization of acetate-capped polymers appears, however, to be catalyzed by surface effects in certain types of infrared cells used for spectral studies. This effect may be caused by end groups, besides acetate, for which there is some spectral evidence. Uncapped polymers have been found to depolymerize quite rapidly under certain conditions, as a result of factors that are not specifically identified at present. Partial depolymerization occurs during storage at low temperatures, and the polymer residues remaining after storage appear to depolymerize much more rapidly in solution at room temperature than the freshly prepared materials. The monomeric impurity formed during storage, or an acid impurity formed by air oxidation of the monomer, may catalyze decomposition; alternatively, the reduced molecular weight may account for the more rapid decomposition. Depolymerization appears to be faster in carbon tetrachloride than in chloroform. The main effort in continuing this research will be to identify the factors responsible for rapid depolymerization of uncapped polymers.

New preparations of heptaldehyde polymers will be required, and we plan to follow basically the same synthesis methods used previously to prepare acetate-capped and un apped polymers. However, in recovering uncapped polymers, we plan to try a change in procedure that may yield purer polymers that can be stored more successfully without decomposition. This change will be to neutralize alkoxide end groups by dissolving the polymer in a nonpolar solvent containing dilute acid, rather than by washing the polymer with an acetone-acid mixture that does not dissolve the polymer and may not affect occluded end groups.

An improvement in storage and sampling conditions for uncapped polymers is desired. We plan to press films for storage, since the polymers may prove to be more stable with a limited surface area in contact with air during sampling. We also plan to store a number of small samples in sealed containers that will be opened when successive samples are desired.

Molecular weights of capped polymers will be determined by vapor-pressure osmometry. Molecular weights of relatively unstable uncapped polymers will be estimated by comparing intrinsic viscosities of capped and uncapped polymers; chloroform solutions at 30°C now appear satisfactory for viscosity studies. Infrared spectra and gas chromatographic analyses will be used in attempts to characterize end groups definitely.

We plan to investigate the following factors that may influence the depolymerization rates of uncapped polymers in solution: type of solvent used; amount of monomer, acid, or oxygen added. We plan to investigate further the possible inhibiting effect of a weak proton donor, such as ethanol, on depolymerization; we plan also to investigate the effect of a strong base, such as butyllithium, which should be an effective initiator of an anionic depolymerization process. The kinetic studies will be conducted initially at room temperature, but later studies on the effect of temperature will be carried out. In the kinetic studies, use will be made of both viscosity and spectral changes to obtain information on rates and on mechanisms of depolymerization (end versus random initiation). Continued use will be made of infrared spectrometry, which has the advantage of yielding fairly specific information on the products of depolymerization but has the disadvantage of poor temperature control. N.m.r. spectrometry appears fairly promising in terms of both specificity and temperature control. Ultraviolet spectrophotometry has been tried briefly and appears capable of showing the conversion of polymer to monomer; since temperature control can be employed, this technique may prove useful.

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VI.   LITERATURE CITED

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